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Improved techniques for washing iron blue suspensions : II. the preparation of o, o'-dichlorobenzidine from o-chloronitrobenzene.

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I. IMPROVED TECHNIQUES FOR WASHING IRON BLUE SUSPENSIONS

II. THE PREPARATION OF O, O'-DICHLOROBENZIDINE FROM O-CHLORONITROBENZENE

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ABSTRACT

I. IMPROVED TECHNIQUES FOR WASHING IRON BLUE SUSPENSIONS

The investigation of several procedures for the speeding of the washing of iron blue suspensions to remove electrolytes is reported. The use of several techniques to coagulate blue particles in the colloidal range to cause more rapid settling was found to be of little value.

A conventional Oliver filter and centrifugal clarifier were found to be unsatisfactory for clearing iron blue suspensions.

Considerable advantage in washing by settling and decantation was obtained with the settling of the blue suspensions in relatively shallow vessels.

A continuous washing procedure was developed whereby the blue suspension was circulated through a cloth tube system where liquid passed through the cloth. The simultaneous addition of water allowed a removal of electrolytes.

II. THE PREPARATION OF O,O'-DICHLOROBENZIDINE FROM O-CHLORONITROBENZENE

The experimental work involved in the development of a procedure for the preparation of o,o'-dichlorobenzidine from o-chloronitrobenzene by liquid phase reduction using zinc and alkali is reported.

Preliminary experiments in the investigation of reactions and general procedure using nitrobenzene to prepare benzidine are described.

The development of the procedures using o-chloronitrobenzene in laboratory and pilot plant preparations is described. A process is presented whereby the o-chloronitrobenzene is reduced in a zinc, zinc oxide, water, alkali, alcohol mixture to the hydrazo compound. This material is separated from the reaction mixture, rearranged, and purified using acid solutions. Detailed instructions and a flow diagram are given together with an estimated raw material cost for the procedure.

I. IMPROVED TECHNIQUES FOR WASHING IRON BLUE SUSPENSIONS

INTRODUCTION

This investigation was undertaken to speed and improve the washing of iron blue suspensions. These suspensions are formed from the oxidation of the reaction products of sodium ferrocyanide, ammonium sulfate, and ferrous sulfate in acid solution. Hence, the blue particles are suspended in an aqueous solution containing several different ions: sulfate, chloride, sodium, iron, and cyanide.

The iron blue pigment, the dried blue particles of the suspension, must be relatively free of electrolytes to insure good color stability. The conventional process for the removal of the electrolytes is the batch washing by decantation of the iron blue suspension. This procedure is essentially one of settling the particles to obtain a clear supernatent liquid that may be decanted, the decantation being followed by reslurrying with fresh make-up water for additional settling. Settling, decantation, and reslurrying are continued until the electrolyte content of the batch has been reduced to a satisfactory value. Excessive time, equipment, and space requirements are the chief objections to the decantation-washing technique.

In studying iron blue suspensions, the characteristics of the blue particles as they exist in the suspension must be considered. The size range varies from particles smaller than the wave length of visible light to particles or agglomerates that may be seen with the naked eye. The particle size range is determined by the striking reaction and the details of the striking procedure. In turn, the range of particle size determines the character of the finished blue pigment.

The general chemical character of the iron blue indicates a material that tends to form hydrates. This tendency is shown quite markedly by the behavior of the iron blue suspension upon concentration; for example, a

solution containing 40 per cent solids is a thick paste. Although the specific gravity of the dried blue particles may be about 1.7, the settling behavior of many of the suspensions indicates an effective specific gravity of the blue particles in suspension considerably closer to 1.0.

The fact that the blue particles exist in solution in a wide range of particle sizes means that a portion of the particles are in the colloidal range where ion adsorption is possible. However, this adsorption should not be permanent. Such behavior may be shown experimentally by the fact that although some adsorption is indicated, a blue suspension may be freed of ions with sufficient washing.

Since the essential purpose of the washing of iron blue suspensions is the removal of electolytes, any procedure whereby the solids in suspension may be separated from the solution containing the electrolyte ions should accomplish the same end as the washing by settling procedures. Filtration of the suspension in a press with subsequent washing in the press has been employed for the removal of electrolytes, but generally this procedure is not desirable because of the high cost of equipment and labor.

From the discussions above it is observed that potentially an increase in the washing rate may be accomplished in several different ways:

1. The settling rate may be improved by a coagulation of the blue particles of the colloidal size.

2. Mechanical devices may be used for the removal of the suspended solids from the suspensions with subsequent washing of the separated solids.

3. The entire suspension may be purified by the preferential removal of the electrolytes.

4. The batch washing of the blue suspension may be speeded by the use

of optimum settling periods and distances.

5. The continuous washing of the blue suspension at the proper concentration, i. e., the continual removal of solution and replacement with fresh water, allows a reduction in the washing time.

The procedures itemized above for the speeding of the washing of iron blue are discussed in detail in the following sections together with the results of investigations along the respective lines.

HISTORICAL

Iron blue was first discovered by a Berlin colormaker named Driesbach in 1704. The first recorded work on the coagulation of iron blue was done by N. Pappada(14) in 1910. Pappada dissolved the precipitate in oxalic acid and purified it by dialysis.

Other methods used to coagulate the suspensions were those of adding electrolytes (1,2,3,5,6,7,8,9,10,12,13,16,17,18), the use of light (15), vibration (11), and coagulation by dilution (4).

The present method of preparing iron blue is given below. Specific weights of sodium ferrocyanide and ammonium sulfate are dissolved in water and heated to 40°C, the pH adjusted with sulfuric acid, and an aqueous ferrous sulfate solution at 40°C and at a definite pH added slowly with good agitation. When addition is complete, the solution is heated to 85°C and sodium chloride and sulfuric acid added. The solution is heated for about an hour after the addition. The resulting suspension is deep blue in color and is usually diluted before the next operation.

Obviously, the iron blue suspensions contain a considerable weight of dissolved material, primarily electrolytes. These electrolytes must be removed if a desirable pigment is to be prepared.

The usual process for the electrolyte removal in the iron blue suspensions is decantation. The suspensions are settled in large open wooden tanks (capacity varying from 7500 to 25,000 gallons) for periods from 14 to 70 hours. Decantation is accomplished by spigots on the sides of the tanks, or siphons. The percentage of total volume decanted varies from 5 to 50 per cent, the highest percentages usually occurring in the initial washes. After decantation, fresh tap water is used to refill the tanks to the original volume.

The suspensions are reslurried by air agitation or by power driven agitators. The suspensions then are allowed to settle, and the cycle is repeated until a satisfactory ion concentration is reached. Ten to fifteen washes are required to obtain this minimum contaminating-ion concentration, or from two to three weeks.

The space requirements, materials in process, and time are considerable for the washing process described above. Since the average hold-up of product for washing is approximately 18 days, eighteen 20,000 gallon tanks are required for a production of 3500 lbs of dry iron blue pigment a day. This production necessitates draining, reslurring, etc., for 18 tanks once a day in addition to the significant tank maintenance.

However, in spite of the many disadvantages of the washing process described above, improvements must be viewed from the economics of the overall cost of iron blue production. Thus many techniques are eliminated because of the relatively great expense involved.

INVESTIGATIONS OF IRON BLUE

SLURRY IMPROVEMENT

A. COAGULATION OF BLUE PARTICLES OF COLLOIDAL SIZE

Sols can be coagulated and precipitated by the proper addition of electrolytes, non-electrolytes, and colloids. In the case of iron blue, electrolytes, unless greatly effective, are not favored because of the ultimate need for their removal. However, a non-electrolyte or colloid that would not seriously influence the character of the blue might be used satisfactorily. Certain colloids in the necessary amounts would be able to stabilize the blue particles in the colloidal range and tend to prevent precipitation; whereas other colloids in the proper amounts can decrease the stability of the particles in the colloidal range and cause precipitation. The range of concentrations over which this latter action can occur depends upon the particular colloids involved.

An experiment to investigate the effect of a colloid on the precipitation of the blue particles in suspension was carried out using two different types of blue suspensions with gelatin as the precipitating colloid. The procedure was to add different amounts of gelatin to the blue suspensions and allow samples of the blue suspensions to settle in 100 ml graduated cylinders. The volume of clear liquid obtained after 23 hours with the different samples is shown in Table I.

When these samples were washed by decanting the clear liquid and refilling with fresh water, those samples showing improvement in amounts settled over the untreated samples continued in their respective positions for several washes. However, as washing was continued, the effect of the gelatin became progressively less.

TABLE I. Comparative Settling of Iron Blue Samples Treated with Gelatin

Sample No.	Gelatin Concentration gm per ml	Volume (ml) Settled in 23 Hours	
		(10)A Blue	(10) Blue
1	0	14	28
2	1.8×10^{-7}	11	28
3	3.6×10^{-7}	16	22
4	9.0×10^{-7}	28	18
5	1.8×10^{-6}	27	24
6	3.6×10^{-6}	12	33

(10)A Blue is a typical slow settling blue and (10) is a typical fast settling blue.

The results of these experiments do show the effectiveness of the gelatin in coagulating the blue particles in the colloidal size range. However, the fact that the effectiveness of the gelatin was not permanent throughout the entire washing of the blue suspensions indicates that the electrolytes influence the behavior of the gelatin as well as the colloidal blue particles, or that gelatin is progressively lost in preference to the blue particles.

The possibilities of greatly improving the settling rates of blue suspensions by the use of colloid addition are not too promising, especially since a rather complicated relation exists between desirable amounts of colloids to be added and electrolyte concentration. Although undoubtedly it would be possible to establish such relations, the value of such work is doubtful not only because of the analyses required for production work, but also because of the variation in the proportion of colloidal blue

particles in the blue suspension from batch to batch.

Since coagulation of the colloidal particles of a blue suspension is the result, among other things, of the approach, contact, and coalescence of the particles, those factors favoring these operations should assist in speeding the settling of the blue suspensions. An increase in temperature causes an increase in the velocity of movement of the particles of a suspension, thereby increasing the possibilities of contact. Actually an increase in temperature improves the settling of iron blue suspensions but hardly enough to justify serious consideration as a means of improving commercial operations.

Many colloidal suspensions resist coagulation because of the electrostatic repulsion of the charges of the particles. It was observed in the literature (18) that iron blue is a suspension of negative complex, thus electrostatical repulsion was possibly stabilizing the suspension. Therefore, procedures for the elimination of the charge on the particles should assist in the precipitation of those colloidal suspensions rendered stable by the charge on the particles. The particles of such a suspension possess no net charge at the isoelectric point. (The isoelectric point, by definition, is that point at which the number of positive charges on the particles is equal to the number of negative charges.) At this point if the particles of the suspension were held apart by electrostatic repulsion, coagulation should occur.

The isoelectric point may be approached by adjusting the pH of the suspension through varying ranges until precipitation occurs. Actually there is precipitation over a range on either side of the isoelectric point.

The variation in the settling at different pH values is shown in Table II.

These data were obtained by allowing samples of iron blue suspension, with the pH adjusted by the addition of $NaHCO_3$, to settle in calibrated 250 ml beakers. The volumes of clear liquid obtained after settling were recorded.

TABLE II. Settling Data for (10)A Blue Suspensions with pH Adjustment with $NaHCO_3$

Number of Washes	pH	Hours Settled	Volume of Clear Liquid (ml)
0_1	1.68	23	85
0	2.62	26	56
0	3.10	26	98
0	3.57	26	86
0	5.65	26	35
2_1	2.30	23	112
2	2.53	20	30
2	2.98	20	37
2	3.30	20	54
2	4.59	20	40

1. No $NaHCO_3$ added to these samples

The results of the variation in the pH on the settling are shown in Table II for unwashed and twice washed blue suspensions. It is interesting to notice that the maximum settling was obtained at a pH of 3.10 for unwashed blue, but at a pH of 2.30 for the twice washed blue. This latter sample was untreated with $NaHCO_3$.

Although these data are not intended to be conclusive, they do show the lack of significant effectiveness of such treatment. This result is expected

in view of the fact that the isoelectric point may be reached not only by pH adjustment, but also by the addition of readily adsorbed anions or cations as required by the colloidal particles involved. Since the iron blue suspensions contain a number of anions and cations, it is hardly expected that an adjustment of the pH would improve materially the settling rate or bring about much coagulation of the colloidal particles.

Another possibility of coagulating the blue particles of colloidal size was by the use of an electric current to assist in the agglomeration of the particles bearing a charge. This possibility was investigated on a laboratory scale by the passage of a current through the blue suspension in a 100 ml cylinder. A carbon electrode was used in the top of the cylinder and a copper screen as the electrode in the bottom of the cylinder. Different currents and voltages were employed for varying periods with comparisons of settling times as the index of effectiveness. A treatment with 3 amperes at 45 volts D. C. for 15 seconds gave the best results. However, at best this procedure gave results no better than those obtained by the other procedures previously described.

Another procedure for the treatment of the small particles of the suspension was the adjustment of the conditions within the system during the formation of the blue particles and afterwards so that crystal growth was favored. In this way the particles that might have been in the colloidal range were allowed to become larger. Although only a few simple experiments along this line were performed, the method is of little practical value because of the change (usually for the worse) in the character of the finished product with change in particle size.

B. MECHANICAL DEVICES FOR THE CLARIFICATION OF THE BLUE SUSPENSION

Filtration can separate the iron blue particles from the liquid of the iron blue suspensions. Generally, a filter press is used for this purpose. When the suspensions are filtered without washing by settling, the blue obtained in the press must be freed of electrolytes and washing in the press is necessary. This procedure is not desirable because of the high operating and maintenance costs. When the suspensions have been washed by settling, filtration in a press ultimately is necessary, but the troublesome press washing is unnecessary.

Several factors contribute to the filtration difficulties. As previously mentioned, a considerable portion of the iron blue particles is in the colloidal range, and therefore the particles are difficult or impossible to retain on filter cloth. In addition, the blue particles as precipitated undoubtedly hydrate to a considerable extent giving a compressible sludge. This compressible sludge during filtration is retained on the filter cloth and tends to fill the openings of the filter cloth so that passage of the liquid becomes increasingly difficult as the operation continues. This action does have the doubtful advantage of retaining even the blue particles in the colloidal range so that those particles passing the filter cloth at the start of the filtration may be recovered by recycling the first filtrate obtained.

Although the usual filtration difficulties were expected, a small Oliver filter was used for filtering the iron blue suspension. Since the partially evacuated filter drum of the unit was continually "cleaned" with a doctor knife during operation, it was considered possible that the

resistance offered by the cloth carrying a relatively thin layer of sludge might be such that reasonable filtration would result. An experimental filtration was carried out wherein 12 gallons of iron blue suspension were filtered using the laboratory Oliver filter. Excellent mechanical operation was experienced, but rather ineffective filtration. The initial blue suspension contained 7.22 per cent total solids, but only 4.05 per cent of the initial solids was retained by 8 oz cotton duck on the filter drum. In other words, the initial blue suspensions contained (7.22/92.78)= 0.078 lb of total solids per lb of water and after filtration the suspension contained (0.078 x (1.00 - 0.0405) = 0.0747 lb of total solids per lb of water. The residue obtained in the use of the Oliver filter was a relatively thick paste containing 40.7 per cent solids.

This experiment rather effectively emphasized the filtration difficulties and the inability of the conventional Oliver filter to handle materials of the character of iron blue.

The centrifuge is another device that may be used for the separation of suspended solids from liquids. Two different series of experiments were carried out using centrifuges.

A laboratory batch centrifuge was used to wash samples of iron blue suspensions. The procedure was to place a sample of the blue suspension in the 8 tubes in the head of the centrifuge and bring the unit to full operating speed (1750 RPM). Frequent inspections allowed a reasonable measure of the time required to move the blue particles to the bottom of the tubes. After a clear supernatant liquid was obtained, decantation and reslurrying with fresh water readied the sample for additional centrifuging. Thus each

centrifuging constituted a washing of the sample.

The centrifuging time to give a clear supernatant liquid for different washings is given in Table III.

TABLE III. Centrifuging Time to Give Clear Supernatant Liquid - Laboratory Batch Centrifuge

Wash Number	Centrifuging Time in Min.
1	25
2	20
3	15
4	15
5	17
6	16

Although good separations were obtained, the solids packed to such an extent that reslurrying was difficult. Lesser centrifuge speeds gave precipitated solids not so densely packed but after a greater time interval.

Another series of experiments was carried out using a small continuous unit, a DeLaval clarifier. This unit was used primarily because of the velocities obtainable (8400 RPM) not because a unit of this design was considered the most desirable.

In the first experiment with this unit 4 liters of (10)A blue suspension were passed through the unit and the effluent liquid analyzed for solids content. The original blue suspension contained 2.7 per cent solids and after one pass through the unit the solids content of the liquid suspension

was reduced to 1.9 per cent. Several additional passes through the unit reduced the solids content to 1.3 per cent. The sludge contained 20 per cent solids.

In a second experiment 2 liters of the blue suspension were diluted with 2 liters of water and the resulting dilute suspension passed through the unit two times. The liquid effluent suspension was found to contain 0.8 per cent solids and the sludge was found to contain 11.2 per cent solids.

In the third experiment with the clarifier 1 liter of the original blue suspension was diluted with 3 liters of water and the resulting suspension passed through the clarifier two times. In this case the solids in the effluent liquid suspension were found to be 0.2 per cent and the residue was found to contain 13.3 per cent solids.

The results of these experiments with mechanical devices show rather clearly the difficulties encountered in conventional filtration and centrifugal clarification of iron blue suspensions. Although some filtration was obtained with the Oliver, the solids passing the filter cloth were entirely too great for practical considerations.

In the case of the centrifugal techniques, good separations are possible as indicated by the batch experiments. However, for good clarification in a continuous unit, speeds considerably above those used (8400 RPM) would be required for good solids recovery without recycling. Even with good solids recovery, only a thick paste results containing a high proportion of liquid.

C. REMOVAL OF ELECTROLYTES FROM BLUE SUSPENSIONS WITH ION EXCHANGE RESINS

As a means of removing electrolytes from iron blue suspensions, the use of ion exchange resins was tried. The techniques of the experiments were relatively simple and involved merely bringing the blue suspensions in contact with the ion exchanger. One series of runs was made by allowing the blue suspension to remain in contact with the resin only long enough for the liquid to pass through a column of the granulated resin. Another series of runs was made by allowing the blue suspension to remain in contact with the resin for one hour.

In preliminary investigations the effectiveness of the treatment was first evaluated by sulfate determinations before and after contact with the ion exchange resin. However, difficulties with accurate analytical techniques indicated the need of more complete analyses.

In using a laboratory batch of iron blue with Amberlite IR-4 (manufactured by the Resinous Products and Chemical Co.), it was found that 67 per cent of the acidity was removed by passing the blue suspension through the resin. When the suspensions were allowed to remain in contact with the resins for one hour, over 99 per cent of the acidity was removed with the sulfate content of the suspensions remaining practically unchanged.

In another experiment a blue suspension was passed through Amberlite IR-4 and then through Amberlite IR-100 with as little "hold-up" time as possible. An analysis of the effluent blue suspension showed no acidity and a 6 per cent reduction in the sulfate ion concentration. However, other experiments showed little consistency in the ability of the exchange resins employed to remove sulfate ions.

In further studies of the effect of ion exchange resins, laboratory settling data were obtained on iron blue suspensions passed through the granulated resin (Amberlite IR-4) in an effort to establish advantages in settling rates from such treatment. Since this resin was effective in reducing acidity, a pH change in the blue suspension so treated resulted. Although a variation in pH by $NaHCO_3$ addition was shown in a previous section to be of little significance in improving settling, comparisons were made in this case where pH changes were brought about by the removal of acidity with the resin as well as by the addition of carbonates.

A volume of blue suspension was passed through Amberlite IR-4 for the removal of acidity. Part of this treated suspension was blended with untreated suspension and the pH of the untreated suspension raised. Then the pH of the blended suspension was further raised by the addition of $NaHCO_3$. This procedure was attempted on blue suspensions in various stages of washing, i. e. after 0,1,2, or 3 washes, which in effect varied the concentration of the foreign ions present. All suspensions used were washed by decantation several times after the initial adjustment of the conditions. All the experiments mentioned above were carried out in calibrated 250 ml beakers. The results of these settling experiments are shown in Table IV.

It is noticed in Table IV that an improvement in settling is realized in comparison with untreated blue by the pH adjustment. However, the improvement is most noticeable in the case of the unwashed blue suspension. Also, this improvement is short lived, lasting for one additional washing. Therefore, although some settling improvement was observed with a pH adjustment, the rapid loss of the advantage certainly indicates no promise for this technique.

In these experiments only a few ion exchange resins were tried with indifferent results, and it is conceivable that other resins might be more effective. Nevertheless, resin costs and the theory of ion exchangers do not hold much promise for this technique of purification of iron blue suspensions.

TABLE IV

Settling Data for (10)A Iron Blue Suspensions
With pH Adjustment by $NaHCO_3$ and Ion Exchange Resins

Sample No.	Number of Washes	Carbonate Added	IR-4 Ion-Exchange Blend	IR-4 Ion Exchange Treatment only	pH	Ml Clear Liquid After 23 hr	% Improvement	% Improvement over Untreated Samples After 1st Additional Wash	After 2nd Additional Wash	After 3rd Additional Wash
1	0			X	3.02	92	8.2	-		
2	0		X		3.00	103	21.2	6.5		
3	0	X	X		4.02	101	18.8	1.9		
4	0	X	X		5.72	101	18.8	1.9		
5	0	X	X		6.82	105	23.6	6.6		
6	0				1.68	85	-	-		
7	1				1.92	88	-	-		
8	1		X		3.09	95	7.9	-		
9	1	X	X		3.59	85	-	-		
10	1	X	X		4.30	91	3.4	-		
11	1	X	X		6.25	88	-	-		
12	1			X	3.79	82	-	-		
13	2		X		2.88	108	-	-		
14	2				2.30	112	-	-		
15	2			X	5.13	89	-	-		
16	2	X	X		3.33	86	-	-		
17	2	X	X		4.32	96	-	-		
18	2	X	X		4.80	104	-	-		
19	2	X	X		6.01	100	-	-		
20	3				2.43	114	-	-		
21	3		X		3.04	102	-	-		
22	3	X	X		3.78	94	-	-		
23	3	X	X		5.28	95	-	-		4.5
24	3	X	X		5.99	95	-	-	No Improvement	18.0
25	3	X	X		6.46	95	-	-		-
26	3			X	5.53	86	-	-		-

D. BATCH WASHING OF BLUE SUSPENSIONS BY SETTLING

In observing the general theory of settling, it is noticed that the dilution ratio, the weight ratio of liquid to solids, has an important effect on the settling. If a very dilute iron blue suspension is poured into a glass cylinder and allowed to settle, a classification is observed, in which the coarsest particles settle to the bottom at a comparatively rapid rate, while the finest particles, settling at a lower rate, remain on top with particles of intermediate sizes between these limits. If all the particles greater than colloidal size have free movement, they will settle at a constant velocity related to other factors by Stokes' law. Stokes' law expressed mathematically is

$$u = \frac{kD^2 (\rho' - \rho)}{\mu}$$

where u is the settling velocity, k a constant, D the particle diameter, ρ' the density of the solid particle, ρ the density of the liquid phase, and μ the viscosity of the solvent through which the particles settle. However, this law will apply only when free settling conditions are approached.

In the case of hindered settling

$$u = k \frac{D(\rho' - \rho)}{\mu}$$

where μ is the viscosity of the system.

As settling proceeds, a gradual clarification takes place, relatively slow in the last stages since very fine particles are present, and a line of demarcation appears between the settling solids and the supernatant liquid.

If the density of the liquid phase is increased by the addition of more solids, a point in concentration is reached where there is a marked decrease in the rate of settling. This is called the point of compression. This

critical concentration is relatively low for iron blue suspensions. The cause of the marked decrease in settling rate, aside from decreasing the driving force (the density differential), by the addition of more solids, is observed in Fig. 1. There is a distinct change in the slope of the per cent total solids versus viscosity curve at about 4 per cent solids. Above this solids content the viscosity increases at a much greater rate than below this value. Since the rate of settling is inversely proportional to the viscosity according to Stokes' Law, and the viscosity proportional to the concentration above 4 per cent solids, any significant increase in the concentration will cause a corresponding decrease in the rate of settling. By the same token, a dilution of the suspensions should cause an increase in the settling rate.

The data for the viscosity - per cent solids curve were obtained by a paddle type Stormer Viscometer. The viscometer was calibrated using glycerine solutions of known viscosity, and observing the time necessary for the paddle to make a fixed number of revolutions in these solutions. A plot of time versus viscosity gave the correlation necessary to obtain the apparent viscosity of the iron blue suspensions at any desired concentration of solids.

In Table V are shown the results of settling samples of iron blue suspensions that were twice as concentrated as those usually used.

Considerably greater quantities of clear liquid were obtained with the more dilute blue suspensions under comparable pH conditions.

This work led to the conclusion that the slow settling of iron blue suspensions was a result of the character of the blue particles and not necessarily because of the presence of particles in the colloidal size range.

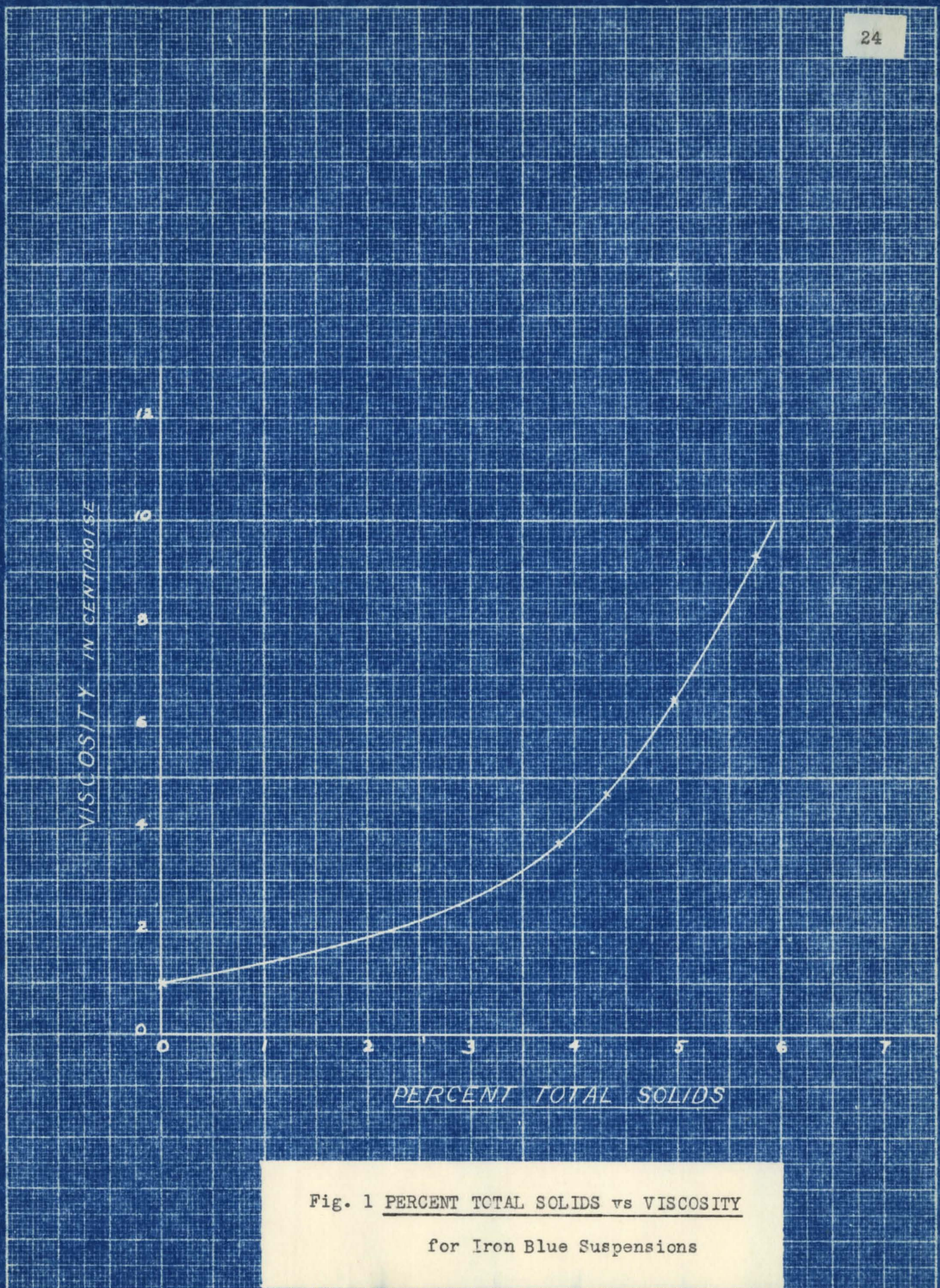

Fig. 1 PERCENT TOTAL SOLIDS vs VISCOSITY

for Iron Blue Suspensions

TABLE V. Settling Data for Concentrated (10)A Iron Blue Suspensions at Various pH Values

Sample No.	pH	Settling Time Hrs	Clear Liquid ml
1	1.50	19	17
2	1.72	22	76
3	3.10	26	56
4	4.33	19.5	66
5	5.64	21	40

pH adjusted with N_aHCO_3

An investigation of the change in concentration of the impurities in the blue suspension with washing was made. An 8 gallon batch of the blue was prepared and divided into four equal parts. One part was used unwashed; the second part was washed once; the third two times; and the fourth was washed three times. Analyses were made on each part to determine the grams of sulfate ion per gram of blue suspension, the per cent dissolved iron, the per cent total solids, per cent suspended solids, per cent dissolved solids, and acidity. With these data, shown in Table VI, the amounts of impurities removed per wash was shown.

The results shown in Table VI indicate little adsorption of the ions investigated since the removal of approximately 50 per cent of the volume of the suspension removes approximately 50 per cent of the ions present.

From the per cent total solids versus viscosity curve (Fig. 1) it was observed that past the point of compression (about 4 per cent solids) the rate of settling fell off rapidly since past this point the viscosity increased more rapidly with increase in solids content. Therefore, as the

blue suspension settled, the layer containing the blue particles continually increased in viscosity and decreased the settling rate. From these considerations it was thought desirable to allow the suspension to settle only a relatively short distance before decanting and washing the suspension. To confirm this reasoning, several laboratory experiments were carried out with unwashed blue suspension.

TABLE VI. Analytical Results from Washed Blue Suspensions

	Unwashed Blue	One Wash	Two Washes	Three Washes
Total Solids (%)	3.4	2.4	1.9	1.7
Dissolved Solids (%)	2.0	1.0	0.5	0.3
Suspended Solids (%)	1.4	1.4	1.4	1.4
Acidity (Normality)	0.0192	0.00955	0.0047	0.0020
Iron (%) -Dissolved	0.014	0.006	0.0028	0.0012
Sulfates (gm SO_4 per gm suspension)	0.00807	0.00732	0.00397	0.00181
Supernatant Liquid Removed in Washing (Per Cent of Original Volume)				
First Wash		47.8	50.5	50.5
Second Wash			48.6	50.5
Third Wash				54.6

One rather simple experiment was the use of one beaker containing a 4 inch depth of blue suspension in comparison with four similar beakers each containing a one inch depth of the suspension. In 24 hours 48 ml of clear supernatant liquid were obtained from the 4 inch depth of suspension while a total of 130 ml was obtained from the four beakers having a one inch depth of blue suspension.

In another experiment of this type, several different depths of blue suspension were settled - 4,8,12,16,30, and 46 inches - with a maximum depth of 6 inches of clear supernatant in the case of the 24, 30, and 46 inch depths in 24 hours, thus rather clearly indicating the advantage of using shallow vessels for the settling of the blue suspensions.

The establishment of (1) laboratory settling rate curves, Fig. 2, (2) the viscosity - solids content curve, and the experiments described above indicated that considerable advantage was to be gained by allowing settling to take place for short periods - 8 hours instead of 24 or longer. It was therefore decided to investigate the possibility of more frequent "draw-offs" in plant operations.

The settling of all blue suspensions at the Kentucky Color and Chemical Company plant were followed for 15 days and the data obtained analyzed. A number of significant items directly and indirectly related to the topic under discussion were noticed in reviewing these data. These items are summarized below.

1. The time allowed for settling varied considerably - from 15 to 70 hours - allowing a good picture of the settling behavior of blue suspensions in plant operations.

2. It was seldom possible to obtain as much as a 50 per cent "draw-off" of clear supernatant liquid in any 24-hour period.

3. The per cent dissolved solids in new batches placed in the tanks during the examination period varied considerably - from 0.568 to 3.980 per cent. There were only two batches in which the initial dissolved solids contents were the same.

4. Considerable variation in the settling of fresh batches of blue

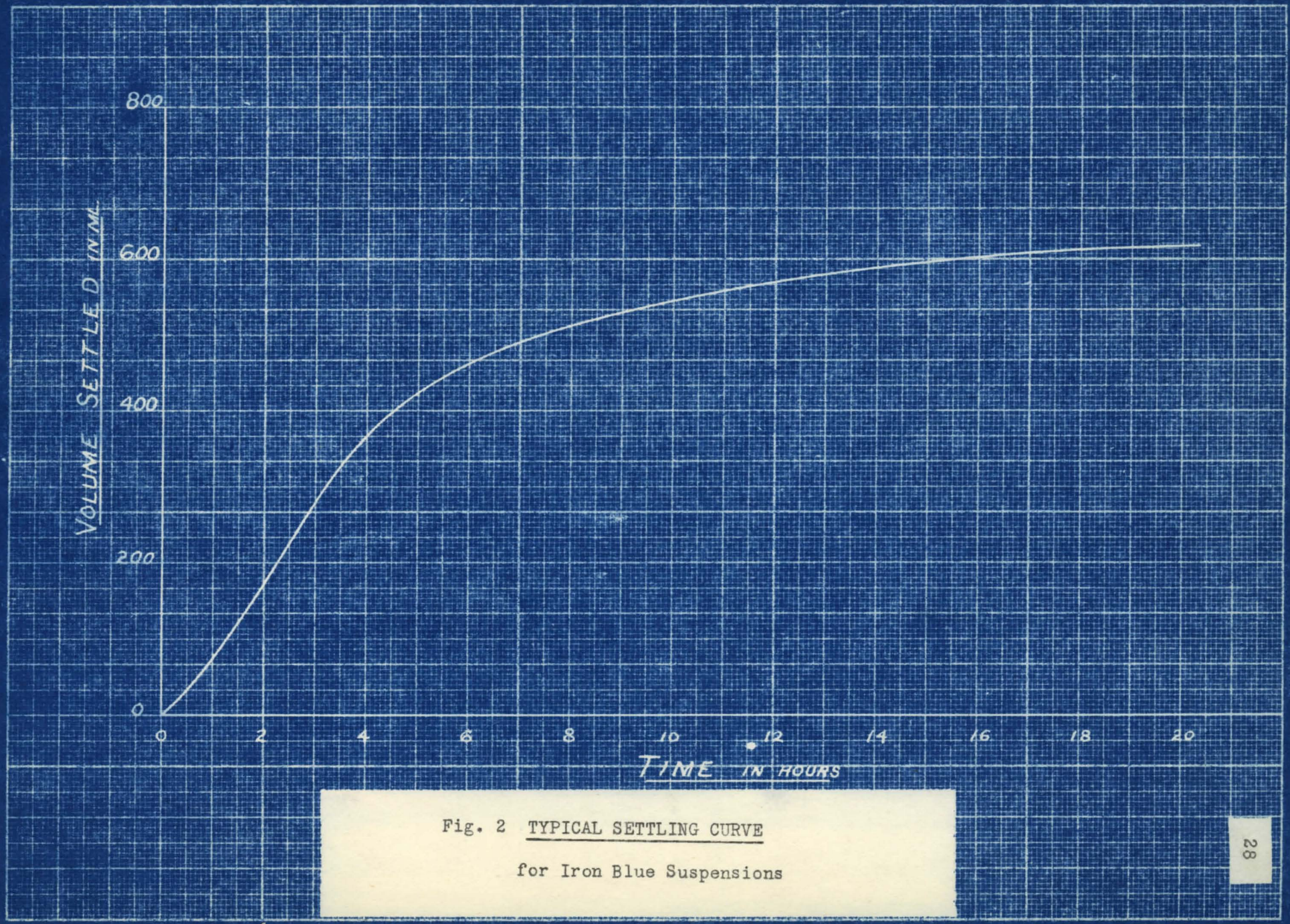

Fig. 2 TYPICAL SETTLING CURVE

for Iron Blue Suspensions

suspension was experienced. This fact would tend to substantiate the variation in the initial dissolved solids contents.

5. Average settling rates calculated for several different washes showed little tendency of a slowing of the settling rates as the washing proceeded.

6. Little difference in the settling behavior of (10) and (10)A - typical fast settling and slow settling blues respectively - was indicated.

These plant studies indicated considerable variation in the character of the blue suspensions from batch to batch. The time required for the decantation in plant work and the considerable variation in blue behavior showed little advantage to be gained from more frequent washing, contrary to the results obtained with laboratory experiments. However, the plant studies confirmed the conclusion from laboratory work that a significant advantage was realized with settlings in shallow vessels.

E. CONTINUOUS WASHING OF IRON BLUE SUSPENSIONS

The use of dialysis procedures for the removal of ionic materials from iron blue suspensions was considered. Dialysis is the term applied to the movement of ionically dispersed materials through a membrane with the retention of particles of colloidal size or above. This phenomenon occurs because of the difference in diffusion rates, concentration, and particle size of the materials on both sides of the membrane.

A laboratory device was constructed to investigate this procedure (Fig. 3). This device was essentially two concentric tubes arranged so that blue suspension would be passed continuously through the annular space between the two tubes. The inner tube was constructed of coarse screening wrapped with filter cloth. No filtration was attempted at first - merely the passage of dissolved material from the blue suspension into the water stream. The blue suspension was pumped through the annular space and water through the inner tube. The pressure on both sides of the filter cloth was equalized by balancing the two pressures, thus theoretically allowing only dialysis to take place and no filtration. In the operation of the unit, it was found practically impossible to balance the blue pressure with the water pressure without constant attention. The results of several experiments indicated that diffusion was at such a low rate as to be of no practical significance in this case.

However, in carrying out the experiments on the unit an unbalancing of the pressures of the blue suspension and the water caused a concentration of the blue suspension (when the blue pressure was above that of the water pressure) or a dilution of the blue suspension (when the water pressure was above the blue pressure). Since continuous liquid removal from the

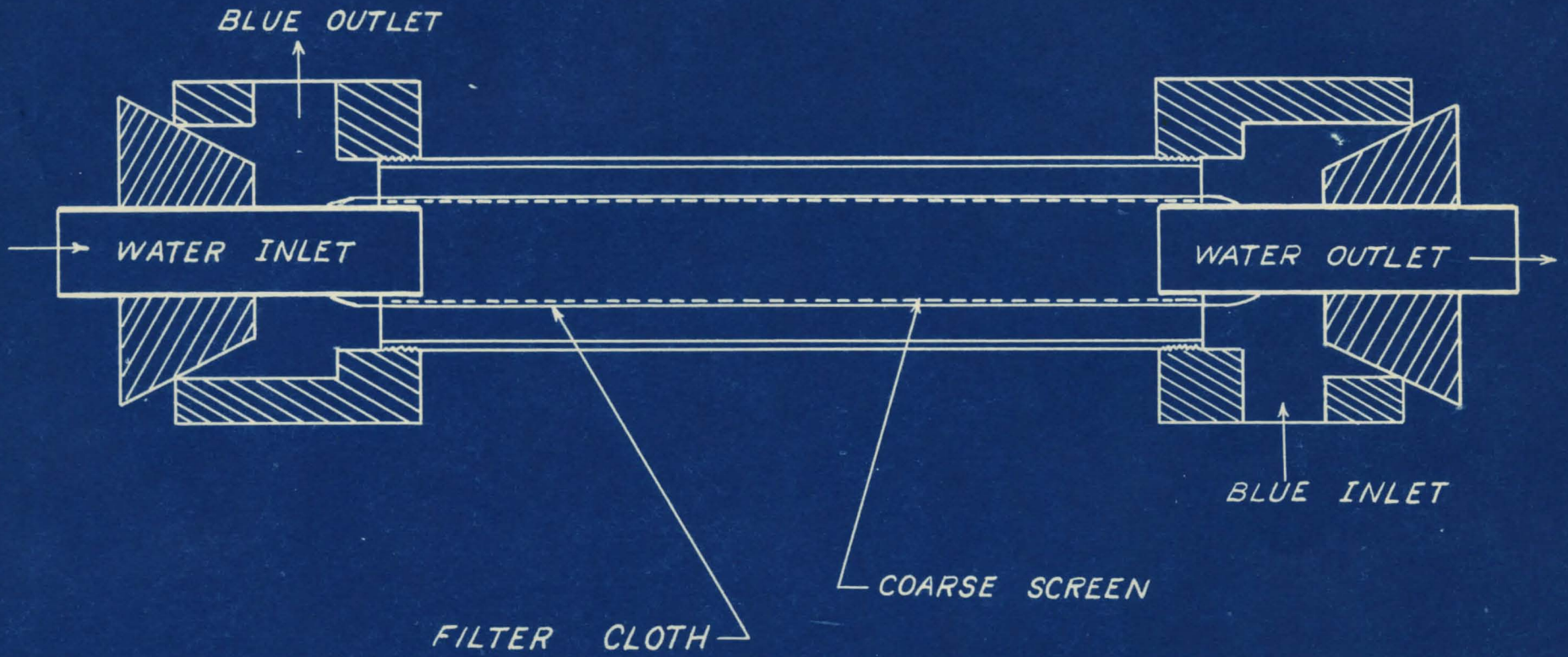

Fig. 3

DIALYSIS APPARATUS FOR ION REMOVAL

blue suspension occured so easily it was decided to capitalize on this characteristic for continuous washing of the suspension.

The experimental procedure was relatively simple and quite effective. As previously stated, the blue suspension was pumped through the annular space between the outer pipe and the porous pipe covered with cloth while water was within the inner pipe. The movement of the blue prevented clogging of the cloth and any pressure differential between the blue and the water was possible with proper adjustment of the water rate within the inner pipe. When the blue became relatively viscous, the procedure was reversed (by increasing the water pressure) and the blue diluted. Then the cycle was repeated with another concentration of the blue.

When the pressure drop between the blue and the water was only 2 lbs per sq in., an average filtration rate of 9.5 lbs of filtrate per hour per sq ft of filter cloth was obtained over a 15-hour period. As expected, drop in the rate was noticed as the blue suspension became more concentrated.

So much promise was indicated by the apparatus that work was continued to establish improved procedures. It was found that with a sufficiently high blue circulation rate to prevent clogging of the cloth, water was unnecessary on the other side of the cloth. This fact indicated the possibility of passing the blue suspension through a cloth tube and allowing the clear liquid to drain off the outside of the tube. Under such condition the apparatus would become a continuous filtering unit.

For additional work a piece of equipment of pilot plant size was constructed so that the blue suspension could be pumped from a tank, through a cloth tube and back to the original tank. A sketch of the unit is shown in Fig. 4.

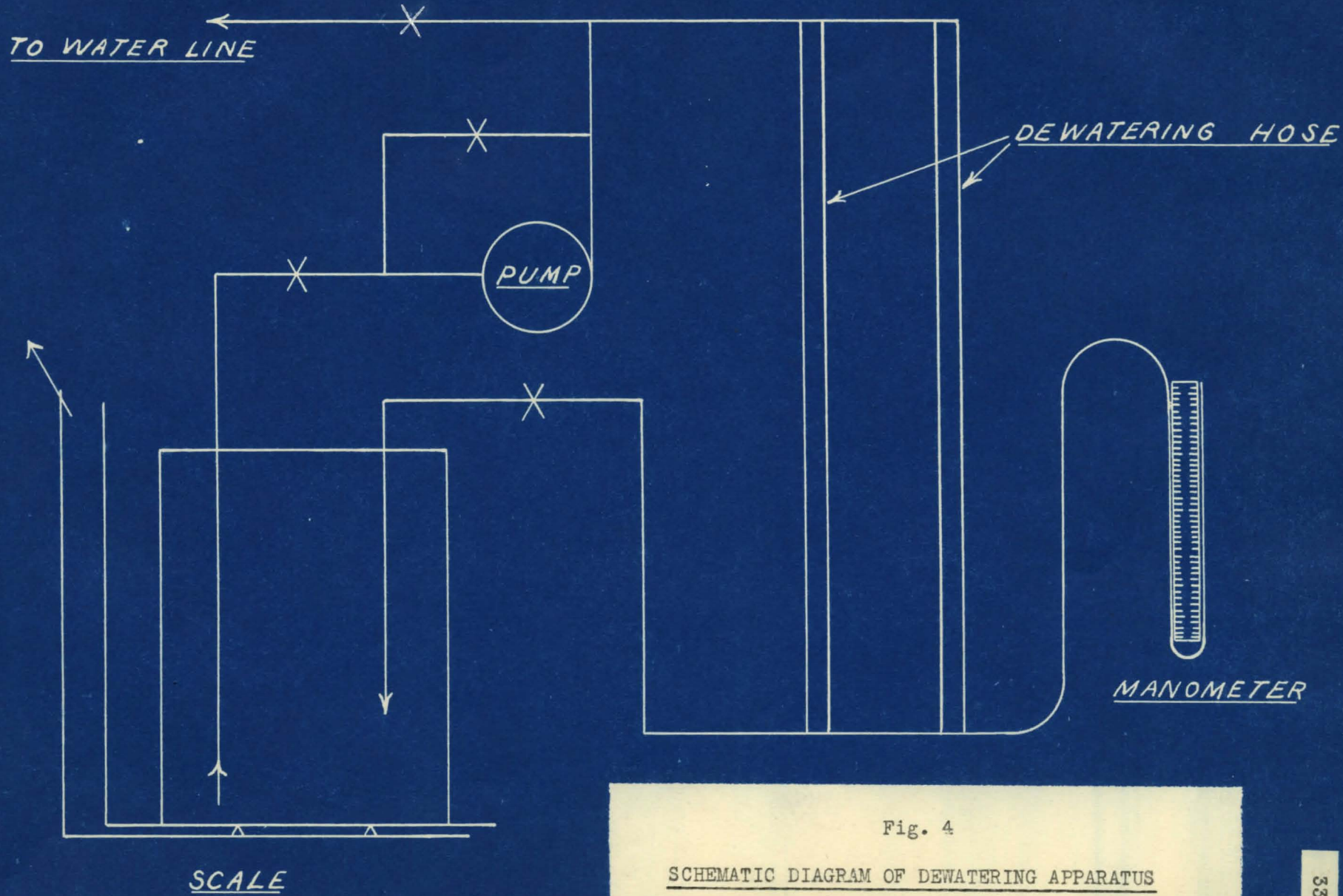

Fig. 4

SCHEMATIC DIAGRAM OF DEWATERING APPARATUS

The blue suspension was pumped from a large crock on a small platform scale through an appropriate piping system, the cotton duck tubing, and back to the original crock. The unit was operated with several different filtering areas and blue circulation rates.

In running the unit, the blue concentration was held constant at 3 per cent suspended solids by balancing the crock on the scale and adding water at such a rate as to maintain balance as liquid passed through the fabric of the cloth tubing. The rate of filtration was determined by recording the weight of filtrate produced in a measured period of time.

A water connection to the unit made it possible to wash the cloth tubes periodically.

A summary of the data obtained from five different runs on the unit is shown in Table VII.

In securing these data it was found in the first run that too much pump capacity was available for the filtration area used. This situation resulted in the clogging of the cloth tube. However, when more filtration area was provided by placing tubes in parallel, this difficulty was eliminated. The object of the other runs was to observe some of the operating characteristics of such a unit.

The data obtained in the five runs reported in Table VII reveal several important items.

1. At moderate circulation rates and pressures an increase in cloth tube area gave an increase in filtration rate (high pump capacity was unnecessary to obtain good results).

2. Only moderate circulation rates were necessary to prevent clogging of the cloth and maintain good filtration rates.

TABLE VII

Dewatering Rate Data
from Pilot Plant Size Unit

Run No.	Total Area sq ft	Length of 1" Tubing ft	Blue Suspension Rate Thru Tubing gal./min.	Filtration Rate gal./hr/ sq ft	Pressure lbs/sq in.
1	1.31	5	10.8	1.64	5.6
2	2.62	10 (2-5ft pieces in parallel)	5.9	2.00	7.1
3	2.62	10(same)	9.0	2.92	11.2
4	7.15	27.3 (2-13.65ft pieces in parallel)	5.9	2.53	6.8
5	7.15	27.3(same)	9.0	3.41	10.1

Note: Blue suspension remained constant at 3 per cent suspended solids.

3. Only moderate pressures were required.

These few runs were not intended to be conclusive but merely indices of the characteristics of such a unit.

The unit was considered expecially promising in view of the fact that it was constructed of standard materials at very low cost.

In operation, a unit of this type allowed the continuous removal of electrolyte-containing filtrate and continuous replacement with fresh water. In this way the blue suspension was washed with a minimum amount of water. It was also possible when washing was complete to concentrate the suspension considerably for the next operation.

SUMMARY AND CONCLUSIONS

The work on this problem has been an investigation of the possible procedures for the removal of electrolytes with the aim of reducing and simplifying the washing of the iron blue suspensions. The important part of the procedures are outlined and discussed briefly below.

1. Coagulation of the Blue Particles of Colloidal Size.

In general it was possible to improve slightly the settling rate by adding a "protective" colloid, i.e., gelatin, and by adjustment of the pH by the addition of $NaHCO_3$. However, because only a portion of the blue particles is in the colloidal range and because the improvement in settling by this means is temporary, the employment of such procedures is not justified.

2. Mechanical Devices for the Clarification of the Blue Suspensions.

The Oliver filter was incapable of removing a sufficient amount of solids from the iron blue suspension.

The batch centrifuge, although not a commercial device, was able to give good settling. However, the time required was considered excessive and the packing of the blue particles was such that reslurrying for additional washes was difficult.

The continuous clarifier operated satisfactorily from a mechanical viewpoint but produced a sludge containing from 85 to 90 per cent water.

It was concluded that these mechanical devices were of little value for improving the washing rate of blue suspensions.

3. Removal of Electrolytes From Blue Suspensions With Ion Exchange Resins.

Amberlite resins were capable of removing acidity and reducing somewhat the sulfate ion concentration. However, high resin costs and the

theory of ion exchangers do not hold much promise for this technique.

4. Batch Washing of Blue Suspensions by Settling.

It was found in these studies that considerable advantage in settling was obtainable using shallow tubs with frequent decantation and reslurrying. A study of the plant settling revealed the difficulties of frequent decantation and reslurrying.

However, the advantages obtainable by the use of shallow tubs for settling are considerable, and not necessarily dependent upon very frequent washing.

It is concluded further that the slow settling of iron blue suspensions results from the character of the blue particles, tendency to hydrate, etc., and not necessarily from the presence of particles in the colloidal size range.

5. Continuous Washing of Iron Blue Suspensions.

The only technique showing real promise in the improvement of the washing of iron blue is the continuous dewatering unit. Filtration rates were sufficiently high to warrant attention and the advantage of the low installation cost is considerable.

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II. THE PREPARATION OF O,O'-DICHLOROBENZIDINE FROM O-CHLORONITROBENZENE

INTRODUCTION

The purpose of this part of the project carried out in the University of Louisville Institute of Industrial Research for the Kentucky Color and Chemical Company was the development of a process, not covered by patents, for the preparation of o,o'-dichlorobenzidine.

The compound o,o'-dichlorobenzidine is one of the intermediates used in the preparation of a class of colors known as benzidine yellows.

Three different procedures that could be used for the preparation of compounds of this type were located in a literature survey:

1. Catalytic hydrogenation of o-chloronitrobenzene
2. Electrolytic reduction of o-chloronitrobenzene
3. Liquid phase reduction of o-chloronitrobenzene

The catalytic procedure was covered rather completely by patents, leaving the electrolytic and liquid phase reduction methods as possible techniques. However, since the electrolytic procedure required considerable specialized equipment, it was decided to concentrate on the liquid phase reduction.

Some patents were found on liquid phase reductions of this type, but these patents were old or pertained to catalyst activation techniques or product separation procedures. Further studies of the literature revealed that there were four main parts to the preparation of this compound by liquid phase reduction:

1. Alkaline reduction of the o-chloronitrobenzene to dichlorohydrazobenzene.
2. Separation of the dichlorohydrazobenzene from the reaction mass from the reduction.
3. Rearrangement of the dichlorohydrazobenzene to the o,o'-dichlorobenzidine.

4. Salt formation by sulfonation to prepare the o,o'-dichlorobenzidine sulfate or reaction with hydrochloric acid to prepare the o,o'-dichlorobenzidine hydrochloride.

Usually some salt of benzidine or its derivatives is prepared in preference to the amine base. In this case, although either the sulfate or hydrochloride was usable, the o,o'-dichlorobenzidine sulfate was favored by the Kentucky Color and Chemical Company.

HISTORICAL

In the literature examined no mention was found of methods of preparing o,o'-dichlorobenzidine sulfate and background information was confined to benzidine and some few derivatives.

Detailed instructions were found for the reduction of nitrobenzene to hydrazobenzene and the rearrangement of the hydrazo compound to benzidine (2,3,4,5,6,7). Groggins reported the use of zinc and iron in strong alkaline solutions for the reduction with subsequent solvent extraction for the removal of the hydrazobenzene from the reduction mixture. He reported the use of alcohol when zinc was used for the reduction and the elimination of the alcohol with the use of iron(4).

Gattermann and Wieland gave the details of a laboratory procedure employing zinc. Alcohol was used for the extraction of the hydrazobenzene and 1:1 hydrochloric acid for the rearrangement in ether solution(3). Weygand presented an electrolytic method for the preparation of hydrazobenzene from nitrobenzene(7). Thorpe and Beilstein recommended the use of alcohol in the liquid phase reduction, separation of the hydrazobenzene by solution of the reduction mass in hydrochloric acid and rearrangement of the hydrazo compound by heating with dilute hydrochloric acid(2,6). Barret presented the same reduction procedure but the separation of the organic portion of the reduction procedure by a 60 mesh vibrating screen in a stream of water. Rearrangement of the hydrazo compound was by dilute hydrochloric acid at 35°C with precipitation as the insoluble sulfate by the addition of sulfuric acid(1).

THEORETICAL

The reduction of o-chloronitrobenzene is accomplished stepwise as shown below.

$C_6H_4NO_2Cl$	O-Chloronitrobenzene
C_6H_4ClN $\diagdown O \diagup$ C_6H_4ClN	Dichloroazoxybenzene
C_6H_4ClN $\|\|$ C_6H_4ClN	Dichloroazobenzene
C_6H_4ClNH $\|$ C_6H_4ClNH	Dichlorohydrazobenzene
$C_6H_4ClNH_2$	Chloroaniline

Obviously, a properly adjusted reduction mixture is required to bring the reduction to the hydrazo stage without going to the aniline form.

For the production of o,o'-dichlorohydrazobenzene, ethanol usually is employed in the zinc-alkali reduction mixture in order to moderate the reducing activity of the system. This reduction of the o-chloronitrobenzene to the hydrazo stage may be represented by the following equation:

(1) $10\ NaOH + 5Zn + 2RNO_2 \longrightarrow RNHNHR + 5Na_2ZnO_2 + 4H_2O$

When zinc is employed for reduction, some of the zinc reacts with the water in the alkaline solution with the evolution of hydrogen, the zinc hydroxide formed dissolving in an excess of the alkali as indicated by the partial equations:

(2) $Zn + 2H_2O \longrightarrow Zn(OH)_2 + H_2$

(3) $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$

Zinc oxide acts as an acid-forming oxide towards the strong alkali, and it is upon this reaction that the solution of zinc in alkali with the evolution of hydrogen depends. Zinc hydroxide is very soluble in an excess of

alkali, but the solution formed is not permanent, an insoluble compound gradually precipitating. The greater part of the sodium zincate is insoluble in the caustic solution and usually is present as a colloidal dispersion in the reaction mixture. If zinc hydroxide is represented as a weak acid, an equilibrium may be expressed as follows:

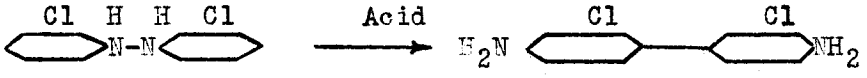
(4) $H_2ZnO_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$

The sodium zincate, in the presence of zinc, is hydrolyzed with the regeneration of sodium hydroxide and zinc hydroxide, which ultimately is converted to the oxide.

(5) $Na_2ZnO_2 + 2H_2O \xrightarrow{Zn} Zn(OH)_2 + 2NaOH$

In actual operation, only 3 to 5 per cent of the amount of NaOH theoretically required according to equation (1) is necessary.

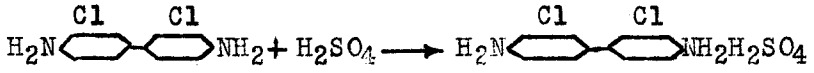
The rearrangement of the hydrazo compound to the benzidine form is brought about in acid solution as indicated by the equation:

(6) 

o,o'-Dichlorohydrazobenzene o,o'-Dichlorobenzidine

Obviously, if the reduction is carried out improperly so that the hydrazo compound is not formed, the above arrangement will not be possible and the desired product will not be formed.

The o,o'-dichlorobenzidine is converted to the sulfate or the hydrochloride by heating with the proper acid as indicated by the equations below.

(7) 

(8) 

EXPERIMENTAL

A. LABORATORY INVESTIGATIONS OF GENERAL METHODS USING NITROBENZENE TO PREPARE BENZIDINE

The first laboratory work was the preparation of benzidine using liquid phase alkaline reduction to study the factors influencing the reduction and rearrangement reactions. Zinc dust was used for the reduction, and the general procedure was as follows:

A mixture of 200 cc of ethyl alcohol, 30 grams of nitrobenzene, and a solution of 15 grams of sodium hydroxide in 35 cc of water in a round-bottom, 3-neck flask, equipped with a mechanical stirrer and a reflux condenser, was heated on a water bath. Zinc dust in portions of 5-6 grams was added while the mixture was agitated and refluxed. Additions of zinc were continued until 65 grams of zinc dust had been added. The mixture was heated until the color of the solution became pale yellow and white crystals formed in test samples cooled to room temperatures. The mixture was diluted with 50 cc of ethanol, heated to vigorous boiling and filtered through a previously heated Buchner funnel to remove the sludge. The filtrate was cooled in an ice-bath to cause crystallization of hydrazobenzene. The crystals were filtered by suction and dried in air at room temperature.

An attempt to estimate the effect of activated zinc was made by heating the zinc with 35 per cent sodium hydroxide solution. The results of these runs are seen in Table VIII, Runs No. 1 and 2.

The effect of the reaction time on the yield was investigated and Runs No. 2, 3, and 4, Table VIII, show that there is no material loss in yield of product in reducing the reaction time from 3.5 to 1.75 hours.

It was found that using the alcoholic filtrate as a solvent materially increased the yield, as seen in Runs No. 4 and 5, Table VIII.

Reduction of nitrobenzene was also attempted by the use of iron filings. The general procedure was that already described for the use of the zinc. In Table VIII, Run No. 6, a coarse grade of iron filings covered with oxide was used. The filings were treated several times with dilute hydrochloric acid, washed with water, and treated with sodium hydroxide solution before use in the reaction. In Run No. 7, a better grade of iron filings containing copper was used, washed free of oil with benzene and ether, treated with dilute hydrochloric acid, washed with water, and boiled in 60 per cent sodium hydroxide. When used in the reaction, the larger particles of iron did not appear to enter into the reaction. The reaction was not carried to completion.

The inefficiency of these types of iron for the reaction was demonstrated in these experiments. (See Table VIII, Run No. 6 and 7).

Hydrochloric acid was used to bring about the rearrangement of hydrazobenzene to benzidine which was precipitated by means of concentrated hydrochloric acid. Attempts were carried out for the conversion of hydrazobenzene to benzidine with the use of ether as a solvent for hydrazobenzene, and without the use of an organic solvent.

For the rearrangement reaction with ether as a solvent, the general procedure was as follows:

Ten grams of hydrazobenzene were dissolved in 100 ml of ether. This solution was added in small portions to 100 ml of ice-cold 20 per cent hydrochloric acid contained in a 500 ml Erlenmeyer flask. The flask was closed by a stopper and the contents were thoroughly agitated after each addition. When all the ether solution had been added, 50 ml of concentrated hydrochloric acid were added and the reaction mixture was allowed to stand in the cold. Crystals were removed by filtration.

TABLE VIII

Results from Experiments on Reduction of Nitrobenzene to Hydrazobenzene

Run No.	Metal Type	Solvent	Weight $C_6H_5NO_2$ gms	Reaction Time and Color Solution	Weight of Products	Yield per cent	Nature of Sludge
1	zinc #40	ethyl alcohol	30	5 hours pale yellow	13.5	61	colloidal-difficult to handle
2	zinc #40 activated	ethyl alcohol	30	3½ hours pale yellow	18.3	82	easily filterable form
3	"	"	30	2.67 hours pale yellow	18.8	85	"
4	"	"	30	1.75 hours pale yellow	18.4	83	"
5	"	filtrate from Run 4	30	1.75 hours pale yellow	22.3	100	"
6	technical oxidized iron filings	ethyl alcohol	30	7 hours dark brown	incomplete reaction	-	colloidal
7	technical iron filings	ethyl alcohol	30	4.5 hours dark brown	incomplete reaction	-	colloidal

These attempts were made, as above, using different periods of time for the reaction. The yield and color of the product are compared in Table VIII, Run No. 1, 2, and 3.

For the rearrangement without the use of an organic solvent, the general procedure was as follows:

Ten grams of pulverized hydrazobenzene was placed in a 500 ml Erlenmeyer flask and 250 ml of 3 per cent hydrochloric acid solution was added. The flask was stoppered and shaken at about room temperature for 30 minutes, then warmed in a water bath at 45-50°C for 30 minutes. The mixture was cooled in an ice-bath and 50 ml of concentrated acid were added. Crystals of benzidine hydrochloride were removed by filtration and dried in air at room temperature.

A comparison of the action of 3 per cent, with the action of 10 per cent hydrochloric acid for the conversion of hydrazobenzene was made. (See Table IX, Runs No. 4, 5, and 6). Dilute acid without the use of an organic solvent produced the best yield.

TABLE IX

Results from Experiments on
Rearrangement of Hydrazobenzene to Benzidine

Run No.	Weight of Hydrazo-benzene gms	Time of Reaction hrs	Percent HCl	Solvent	Yield of Product gms	Percent Yield	Color of Product
1	10	½	20	ether	7.5	54	pale yellow
2	10	1 3/4	20	ether	11.6	84	almost white
3	10	17	20	ether	10.1	72	light tan
4	5	1	3	-	6.2	90	almost white
5	10	1	10	-	11.5	83	green
6	10	1	3	-	13.5	97	very light beige

Upon completion of the preparation of benzidine just described, the liquid phase reduction of o-chloronitrobenzene to o, o'-dichlorohydrazobenzene with subsequent rearrangement to o, o'-dichlorobenzidine was undertaken.

Experiments were performed on the reduction of o-chloronitrobenzene by means of zinc dust in alkali solution, using different reaction mediums, alcohol, water, alcohol-water, and benzene-water.

With alcohol as a medium, the general procedure was that used in the study of the preparation of hydrazobenzene except that o-chloronitrobenzene was used in place of nitrobenzene and New Jersey No. 22 zinc was used in place of No. 40 mesh zinc. (See Table X, Runs No. 1,2,3,4,and 5.)

The average yield for No. 1, 2 and 3 was 45.5 per cent. The use of the filtrate from Run No. 3 in No. 4 resulted in an increase in the yield from 45.5 to 70 per cent.

The result of a 10 per cent increase in the concentration of the sodium hydroxide was a decrease in yield from 45.5 to 37.5 per cent.

With water as a medium, the general method, based on a report in Chemical Abstracts (5), was as follows:

15.75 grams of o-chloronitrobenzene was strirred for 3-4 hours with 14 grams of zinc dust and 1.9 grams of sodium hydroxide (50 per cent solution) at 75°C. The reaction mass was diluted with water (3 parts) and treated with 18 grams of 10 per cent sodium hydroxide solution at 65-70°C until a sample extracted with benzene was light yellow.

Two runs were made using water as a medium, and attempts were made to separate the dichlorohydrazobenzene product from the inorganic sludge by two methods:

(1) The addition of dilute sulfuric acid to convert the hydrazo

compound to o, o'-dichlorobenzidine sulfate, and (2) by extracting the product from the sludge by means of ethanol and subsequently crystallizing dichlorohydrazobenzene.

The results of the sulfuric acid were doubtful because the presence of a considerable quantity of unreacted zinc caused a reaction with the acid, which appeared to destroy a large portion of the dichlorohydrazobenzene. (See Table X, Run No. 9).

Extraction of the hydrazo compound with ethanol gave dichlorohydrazobenzene in a good yield. (See Table X, Run No. 10).

The use of benzene and water as a medium was attempted, using the same method as previously described, except that benzene (10 cc) was added for the first stage of the reaction, and the remainder of the benzene was added at the end of the reaction to extract the product. Preliminary attempts to recover the product from the solvent failed. (See Table X, Runs No. 7 and 8). A workable procedure with benzene as an extracting agent is described in a later portion on separation.

The procedure for the use of alcohol and water as a reduction medium was the same as described for the use of water alone, except that alcohol was added for the first stage of the reaction. No yield was reported as no attempt was made to convert the moist product directly to o, o'-dichlorobenzidine. See Run No. 6.

The separation of the dichlorohydrazobenzene from the reaction mixture was the next problem to be investigated. There were two procedures considered workable:

(1) extraction of the organic material and (2) extraction of the inorganic materials of the reduction mixture.

TABLE X

Results of Experiments for the
Preparation of O, O'Dichlorohydrazobenzene

Run No.	Weight of O-chloro-nitrobenzene	NaOH added gms	Zinc added gms	Medium volume ml	Reaction Time	Per cent Yield
1	37.8	15	65	alcohol 200	8	40
2	28.5	11.2	88	alcohol 150	4	47
3	18.9	7.5	50	alcohol 100	8.5	49
4	18.9	7.5	45	Filtrate No. 3 100	3	70
5	15.75	8.2	45	alcohol 100	4.5	37.5
6	15.75	3.7	35	80 alcohol 90 water	8	Product converted
7	15.75	3.7	20	10 benzene 90 water	1	Product converted
8	15.75	3.7	20	10 benzene 75 water	5.5	Product converted
9	15.75	3.7	30	water 60	7	Product converted
10	15.75	3.7	30	water 60	7	59

The inorganic portion could be taken into the solution by acids and the organic portion could be extracted by solvents, such as benzene, alcohol, etc. The use of organic solvents was used initially, and was introduced into the reacting vessel after reduction was complete. However this technique proved to be unsatisfactory, since both the alcohol and the benzene emulsified with the

inorganic portions giving incomplete separations.

Since it was requested by the Kentucky Color and Chemical Company that the use of solvents be eliminated if possible because of high costs and handling difficulties, work on other separation techniques was undertaken.

In the early stages of the problem, the separation and rearrangement were done in one step using concentrated hydrochloric acid, since sulfuric acid did not seem to give the desired results. It was later revealed that the dilute sulfuric acid did cause rearrangement, but only under certain constraining conditions. Therefore, either concentrated hydrochloric acid or dilute sulfuric acid could be used to effect a separation.

The rearrangement of dichlorohydrazobenzene to o, o'-dichlorobenzidine in both hydrochloric and sulfuric acids was investigated, with and without the use of solvents.

The first attempt at rearrangement was with cold 3 per cent hydrochloric acid as described previously, and the yield of o, o'-dichlorobenzidine hydrochloride from the hydrazo form was 77 per cent. Rearrangement was then attempted with dilute sulfuric acid. A sample of dichlorohydrazobenzene mixed with 50 per cent sulfuric acid at 10-15°C, was allowed to stand in an ice box for 48 hours, then heated to 60°C for $1\frac{1}{2}$ hours gave a yield of 90 per cent of o, o'-dichlorobenzidine. A sample also was treated with 3 per cent sulfuric acid for 3 hours, followed by the addition of 50 per cent sulfuric acid, but no product was obtained.

Rearrangement by means of an organic solvent and hydrochloric acid was tried. An alcoholic solution of hydrazo product, treated with concentrated hydrochloric acid at boiling temperatures, produced a yield of 100 per cent of dark colored crystals. Recrystallization of the dark colored product

from acidulated water and treatment with caustic solution resulted in the formation of crystals melting at 134-5°C. Reported melting point of o, o'-dichlorobenzidine was 133°C.

The use of ether and ice-cold 1:1 hydrochloric acid for rearrangement was as follows:

The hydrazo compound was dissolved in a minimum amount of ether, and added dropwise to ice-cold 1:1 hydrochloric acid. After addition, the reaction mixture was allowed to stand in an ice bath before filtering off the greyish tan benzidine derivative. The lapse of time between the rearranging and filtering of the crystals was varied from $\frac{1}{2}$ hour to overnight. The increase in time increased the yield of the benzidine from 43 per cent with $\frac{1}{2}$ hour standing to 90 per cent of the theoretical with the overnight standing.

Since it was reported in the literature that both cold concentrated hydrochloric (2) and hot dilute hydrochloric acid (4) would cause rearrangement, and it was discovered that "concentrated" (50 per cent) sulfuric acid would cause conversion, a reduction was made and the hydrazo form was divided into four equal parts. Each portion was to be rearranged by one of the following solutions:

(1) cold concentrated hydrochloric acid

(2) hot dilute hydrochloric acid

(3) cold concentrated sulfuric acid

(4) hot dilute sulfuric acid

The cold solutions were to stand for $3\frac{1}{2}$ hours and the dilute acid solutions were heated for 1 hour. The results are shown in Table XI.

TABLE XI

Results of Various Rearrangement Solutions

Run No.	Acid used	Concentration per cent by weight	Yield per-cent	Melting Point °C	Purity per cent
1	HCl	17	19.4	215	73
2	HCl	35	7.2	210	100
3	H_2SO_4	91	12.8	220	88
4	H_2SO_4	30	—	95	—

The hot dilute sulfuric acid did not convert the hydrazo product, as the other three solutions did. The use of hot dilute hydrochloric acid gave the highest yield, but the lowest purity.

B. LABORATORY EXPERIMENTS TO ESTABLISH OPTIMUM REACTION PROPERTIES, CONCENTRATIONS, TEMPERATURES, AND PROCEDURES

There were numerous variables investigated in the alkali-zinc reduction of o-chloronitrobenzene to dichlorohydrazobenzene. They were (1) method of addition of reactants, (2) various grades of zinc, (3) concentration and amount of sodium hydroxide to be used, (4) consistency of reaction mass during reduction, (5) amount of alcohol to be used, and (6) the significance of zinc oxide present in the reduction mixture.

A series of 28 runs were made, see Appendix Table XVI, resulting in the establishment of a procedure employing ethyl alcohol with o-chloronitrobenzene, sodium hydroxide, zinc, zinc oxide, and water. The procedure was the addition of all the o-chloronitrobenzene and alcohol to the reaction vessel, and heating to refluxing temperature. The other constituents, the zinc (granular or dust) zinc oxide mixture and caustic solution (35 per cent), were added slowly and as continuously as possible over a 4-6 hour period. The reaction mass was refluxed by application of external heat when necessary. Water was added as needed to keep the reaction mixture fluid. The reaction was continued after the addition of all reactants until a light colored solution was obtained. When this color change occurred and samples drawn from the reaction vessel proved to be the hydrazo compound, the reaction was complete.

The reactants used for the reduction of 1 mole of o-chloronitrobenzene (157.5 gms) to dichlorohydrazobenzene were

3.36 moles (220 gms) of zinc

2.18 moles (100 gms calculated as 100 per cent) ethanol

1.25 moles (50 gms) sodium hydroxide

0.25 moles (20 gms) zinc oxide

and an amount of water varying from 12 moles (216 gms) to 40 moles (720 gms)

as needed to maintain fluidity.

The alcohol present served three purposes: (1) it formed a ternary system with the o-chloronitrobenzene and the water ; (2) reduced the reduction tendency of the zinc; (3) and served as a temperature control. Some hydrazo product was formed when alcohol was not used in the reduction mixture, but the presence of alcohol increased the yield.

It was reported in the literature (4) that less sodium hydroxide could be used for the reduction. However, too little sodium hydroxide was considered undesirable since inorganic zinc salts were insoluble in water but soluble in caustic solution. Also the sodium hydroxide promoted the reactivity of the zinc maintaining good reduction conditions over a greater portion of the reaction period.

Experimentation was done with the preparation of dichlorohydrazobenzene by alkaline reduction with iron. Five runs were performed using the same procedures that were employed with zinc and water as the medium. The reduction was carried out in two stages. In the first stage concentrated aqueous alkali (50 per cent solution of NaOH), o-chloronitrobenzene, and activated iron filings were reacted for several hours.

For the second stage of the reaction, diluted alkali was added, and the reaction was continued for a considerably longer time. The product of the reduction was separated by filtration and treated with hydrochloric acid for conversion to the benzidine derivative. The yield in every case was neglible. (See Table XII, Runs 1-6). The iron was activated by heating to boiling with 30 per cent NaOH solution.

TABLE XII

Tabulated Conditions of Experiments for the Preparation of O, O'-Dichlorobenzidine Using Iron for the Reduction

Run No.	O-Chloro-nitro-benzene moles	NaOH Used gms	Volume Water ml	Iron Used gms	Reduction time in hours
1	0.1	8	225	60	5
2	0.1	12	260	60	8
3	0.1	40	260	15	8
4	0.1	40	260	15	8
5	0.1	12	260	130	8
6	0.1	160	130	200	9

It was considered necessary to obtain solubility data for o, o'-dichlorobenzidine in sulfuric acid solutions in order to facilitate the precipitation of the sulfated product from sulfuric acid. Previously the sulfonated product was precipitated by neutralization of the acid solution with sodium hydroxide solution.

Several methods of determining the solubility were investigated before a workable one was found. This procedure was as follows:

A sulfuric acid solution of known composition, by specific gravity, was saturated with o, o'-dichlorobenzidine sulfate, at various temperatures. A weighed sample of saturated solution was removed at each desired temperature. This sample was then neutralized with standard sodium hydroxide by titration. The neutralization resulted in a slurry of o, o'-dichlorobenzidine base and water, and small amounts of sodium sulfate. The slurry was filtered and the

sodium sulfate washed from the o, o'dichlorobenzidine base with hot water. The base was then dried and weighed. Amounts of o, o'-dichlorobenzidine sulfate present were calculated from the weight of o, o'-dichlorobenzidine base multiplied by a ratio of molecular weights. This weight subtracted from the weight of total sample gave the weight of acid solution present. From the weight of o, o'-dichlorobenzidine sulfate present in a known amount of acid, the weight per 100 grams of acid solution could be calculated at a specific temperature (See Figs. 5 and 6). From the volume of standard base required, a check on the data was possible.

Identification of the synthesized product by comparison of physical properties of a known sample of o, o'-dichlorobenzidine hydrochloride was investigated. The two samples were tested by (1) comparing their appearance, (2) comparing their melting points, (3) converting each to the benzidine base, and (4) determining the melting points. Similar comparisons were made with the sulfated product. All synthesized material could be classified with the use of Table XIII.

The purity of the synthesized acid products was calculated by titration with sodium hydroxide. The procedure was to wash from the crystals, with a minimum amount of water, any free acid, and then dry the crystals. A weighed dry sample (about 1 gram) was then suspended in water and titrated with standard sodium hydroxide. When the inaccurate first end-point was reached, the sample was heated to boiling for 5 minutes and again titrated until the color change lasted for 1 minute. This was the final end-point and from the weight of sample used, the volume of standard base used, and the equivalent weight of o, o'-dichlorobenzidine sulfate, the purity was calculated.

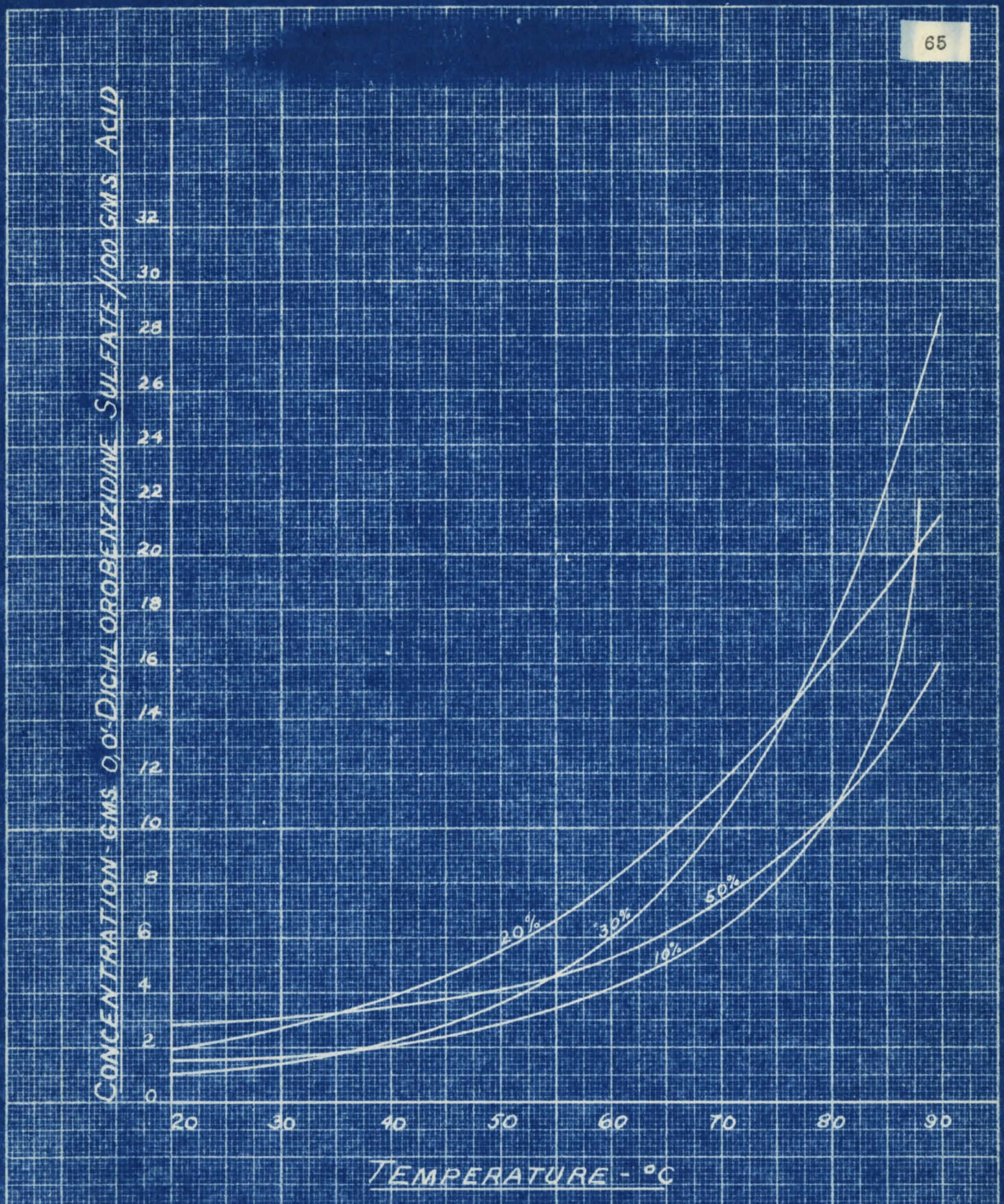


Fig. 5 SOLUBILITY of O, O'-Dichlorobenzidine Sulfate in Sulfuric Acid at Constant Acid Concentration

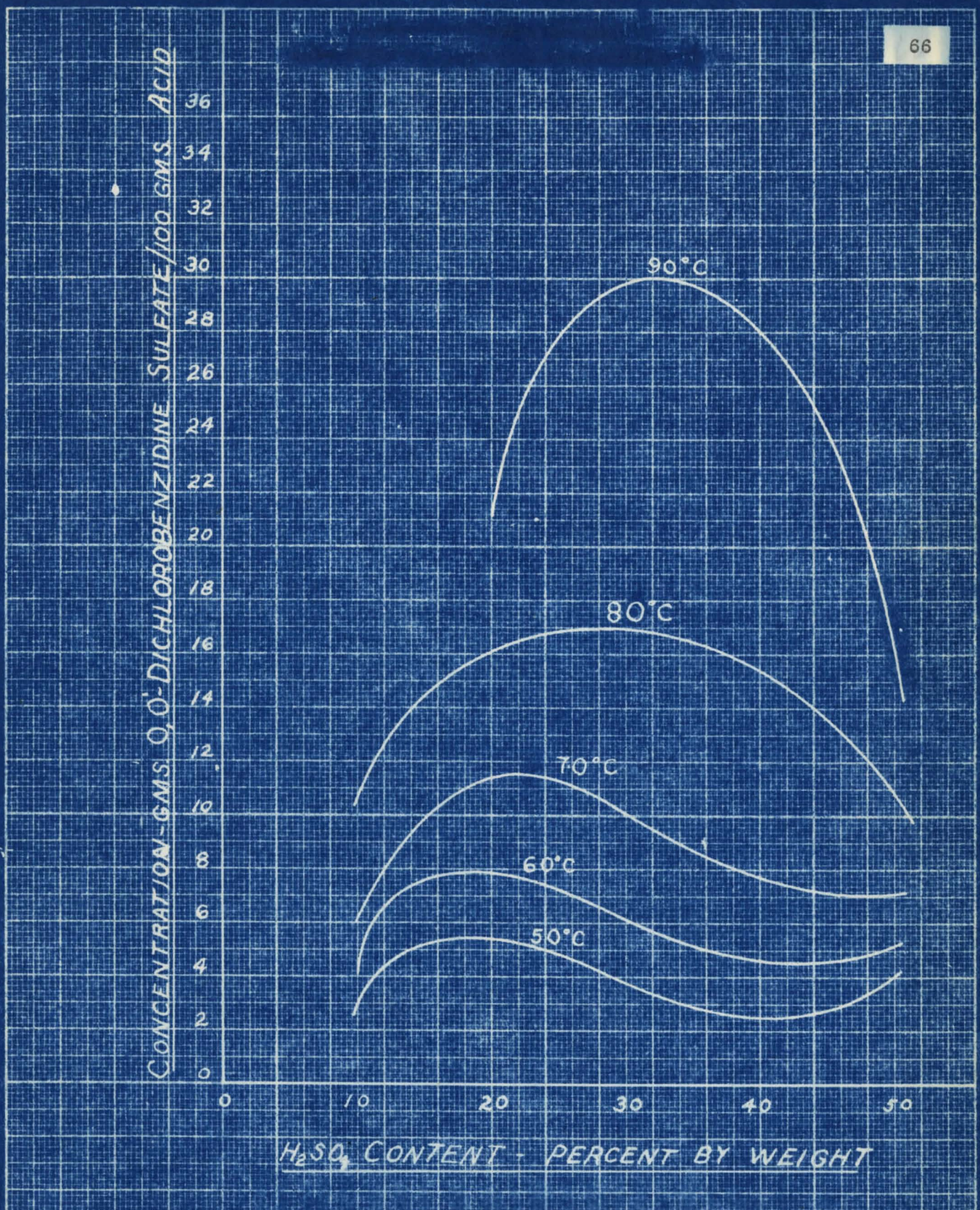


Fig. 6 SOLUBILITY of O, O'-Dichlorobenzidine Sulfate in Sulfuric Acid at Constant Temperature

TABLE XIII

Physical Properties of Compounds
Related to 0, 0'-Dichlorobenzidine

Compound	Molecular Weight	Melting Point °C	Form	Solubility		
				H_2O	Alcohol	Ether, etc
Azobenzene	197	57-68	orange needles	i	sol.	s. eth. s.benz
Azoxybenzene	198	36	R., yellow	i	17.5^{16}	v.s. eth.
Hydrazo-benzene	184	131	R., yellowish-white. From alcohol	n.sl.s.	3.95	s. eth. i. acetic acid
Benzidine	184	116-129	White to reddish powd. or leaf from water	1^{100}	sol.	2.2 eth.
Dichloro-azobenzene	268	75-80	Reddish needles	i	sl.sol.	sl. sol.
Dichloro-hydrazobenzene	253	—	white to tan	-	-	-
0, 0'-Dichloro-benzidine hydrochloride	289	155-165#	grey homogeneous mass	i	i	i
0, 0'-Dichloro-benzidine sulfate	351	210-220#	beige clayish appearing material	i	i	i

C. PILOT PLANT PREPARATIONS OF O, O'-DICHLOROBENZIDINE

Several of pilot plant preparations of o, o'-dichlorobenzidine were were carried out in the course of this investigation. In general, these runs were used as verifications of procedures established in the laboratory work.

All the pilot plant preparations were carried out in a 10 gallon, jacketed iron reactor equipped with a reflux condenser and agitator.

When a laboratory procedure that seemed satisfactory was developed, the procedure was moved to the pilot plant equipment. With this practice a number of laboratory operations were found to be unworkable on the larger scale, and steps to correct them were taken. Thus, in glassware it was found that the reduced material could be extracted with benzene. However, when this practice was tried on a pilot plant scale, emulsions that were obtained resulted in a considerable loss of product. This result led to the development of the acid technique for the separation of the organic material from the reduction mixture. For a tabulation of the amounts of constituent chemicals used and the results of the pilot plant runs, see Appendix, Table XVII.

SUMMARY AND CONCLUSIONS

This section is divided into several parts. The conclusions from the preliminary investigation of the preparation of benzidene from nitrobenzene is presented as well as the conclusions from the investigation of the preparation of o, o'-dichlorobenzidine.

Detailed instructions also are given for the preparation of the o, o'-dichlorobenzidine sulfate together with an estimated raw material cost at various yields.

The conclusions drawn from the work with the preparation of benzidine from the alkaline reduction of nitrobenzene are:

1. The use of activated zinc dust for the nitrobenzene in alcoholic alkaline solution reduces the time necessary for the completion of the reaction, and changes the nature of the sludge from colloidal to an easily filterable form.

2. Yields obtained at different reaction times indicate that the practical completion of the reaction is shown by the appearance of a pale yellow color in the solution.

3. The alcoholic filtrate from one run may be used to advantage in another run.

4. Unused zinc is the sludge may be recovered to be used again.

5. Dilute hydrochloric acid without the use of ether is more efficient for the conversion of hydrazobenzine to benzidine than dilute hydrochloric with ether used as a solvent for the hydrazobenzene.

The concentration of the acid for rearrangement should be less than 5 per cent by weight.

Conclusions drawn from the work on the reduction of o-chloronitrobenzene

to dichlorohydrazobenzene by means of zinc in alkaline solution and subsequent processing of o, o'-dichlorobenzidine sulfate are:

1. Alkaline reduction of o-chloronitrobenzene by means of zinc may be carried out in alcohol, benzene, or water medium.

2. The best recovery of product is made when the reaction is carried out in alcohol-water or water medium.

3. The best yield is obtained by using as a reaction medium the alcoholic filtrate from a previous run.

4. Increase in concentration of alkali causes a decrease in the yield when the reaction is carried out in alcohol-water as a medium.

5. The yield is increased when small amounts (5-10 per cent) of zinc oxide are present in the zinc used for the reduction.

6. Lesser volumes of alcohol than those recommended result in a lowering of the yield.

7. A better yield is obtainable when the reduction is carried out in a thin slurry than when a thick paste is used.

8. The total reaction time is from 5-8 hours, and the yield is not a function of reaction time after about the first 4 hours.

9. Good agitation is essential to the success of the reduction.

10. The use of temperature greater than 120°C in the reduction results in decomposition of the product or side reactions.

11. Solvent extraction of the hydrazo product from the reduction mass can be accomplished with benzene, alcohol and other organic solvents. Hydrochloric or sulfuric acid can be used to dissolve the inorganic materials present, thus affecting a separation. This latter process should be carried out in the cold.

12. The rearrangement of dichlorohydrazobenzene to o, o'-dichlorobenzidine is affected by concentrated cold or hot hydrochloric or sulfuric and cold or hot dilute hydrochloric. The use of the dilute acids gives the larger yields.

13. There is considerable solubility of the dichlorobenzidine hydrochloride in dilute hydrochloric acid.

14. Conversion of dichlorohydrazobenzene to the hydrochloride of o, o'-dichlorobenzidine may be carried out in alcoholic solution at boiling temperatures with hydrocloric acid. The conversion also will take place in cold ether solution by the use of concentrated hydrochloric acid, but the yield is lower than with the use of the dilute acid alone.

15. The dichlorobenzidine base or hydrochloride can be sulfonated by heating the material in dilute sulfuric acid. If the hydrochloride form is used, the hydrogen chloride is replaced by the sulfuric acid group.

16. The sulfated product is soluble in dilute sulfuric acid, and to avoid partial neutralization of the solution for precipitation, the solubility curves (Figs. 5 and 6) should be followed when calculating the amount of acid necessary to sulfate a quantity of base. If the curves are used, the sulfate product should precipitate upon cooling of the acid solution of the product.

17. The maximum solubility of o, o'-dichlorobenzidine sulfate in sulfuric acid varies with temperature and acid content. As the temperature is increased, the maximum moves from about 15 per cent at 50°C to 30 to 35 per cent at 90°C (See Fig. 6). The concentration of acid solution to be used in dissolving the o, o'-dichlorobenzidine sulfate is

30-35 per cent sulfuric acid solution by weight.

18. The absence of significant yields in the series of experiments using iron for the reduction is due to the inactivity of the iron and the caustic under the conditions used.

A summary of the process as developed is presented below accompanied by an estimate of the cost of materials for the preparation of o, o'-dichlorobenzidine sulfate.

The four main steps involved in the preparation of o, o'-dichlorobenzidine sulfonate are:

1. Reduction of o-chloronitrobenzene

2. Separation of organic materials from inorganic constituents of the reaction mixture.

3. Rearrangement of the hydrazo compound to the benzidine form.

4. Sulfonation of the benzidine base.

The quantities of the reactants used for the reduction of 1 mole of o-chloronitrobenzene (157.5 gms) to dichlorohydrazobenzene are:

3.36 moles (220 gms) of zinc

2.18 moles (100 gms calculated as 100 per cent ethanol) of ethanol

1.25 moles (50 gms) of sodium hydroxide

0.25 moles (20 gms) of zinc oxide

and an amount of water varying from 12 moles (216 gms) to 40 moles (720 gms).

A flow sheet and a more detailed description of the preparation of o, o'-dichlorobenzidine sulfate follows.

DETAILED INSTRUCTIONS FOR THE PREPARATION OF O, O'-DICHLOROBENZIDINE SULFATE

Reduction Procedure

1. Add all o-chloronitrobenzene and alcohol to be used.

2. Add the zinc-zinc oxide mixture and the aqueous alkali solution (35 per cent) slowly and as continuously as possible over a six-hour period. Heat is added throughout most of the reaction time.

3. Add water as needed to keep the reaction mixture fluid.

4. Continue reaction after the addition of all reactants until a light color of the reacting mass is obtained. When this color change occurs, samples should be taken and treated with hydrochloric acid in the laboratory. The melting point of the product should be determined. If the desired reduced product is present, dichlorobenzidine base or hydrochloride will be produced, which melt at 131°C and 160-165°C respectively. The reaction time is usually from seven to nine hours.

Separation of O, O'-Dichlorohydrazobenzene

5. A volume of dilute sulfuric acid (30 per cent), approximately 500 ml of dilute acid for 1 mole of o-chloronitrobenzene used, and enough ice to keep the temperature at about 20°C is added to the reduced material.

6. Filter and discard the inorganic filtrate.

Rearrangement to O, O'-Dichlorobenzidine

7. Heat the residue for $1\frac{1}{2}$ hours with dilute (20 per cent) hydrochloric acid, 400 cc per mole of o-chloronitrobenzene. Cool the slurry, dilute, and filter. The residue contains o, o'-dichlorobenzidine hydrochloride and impurities.

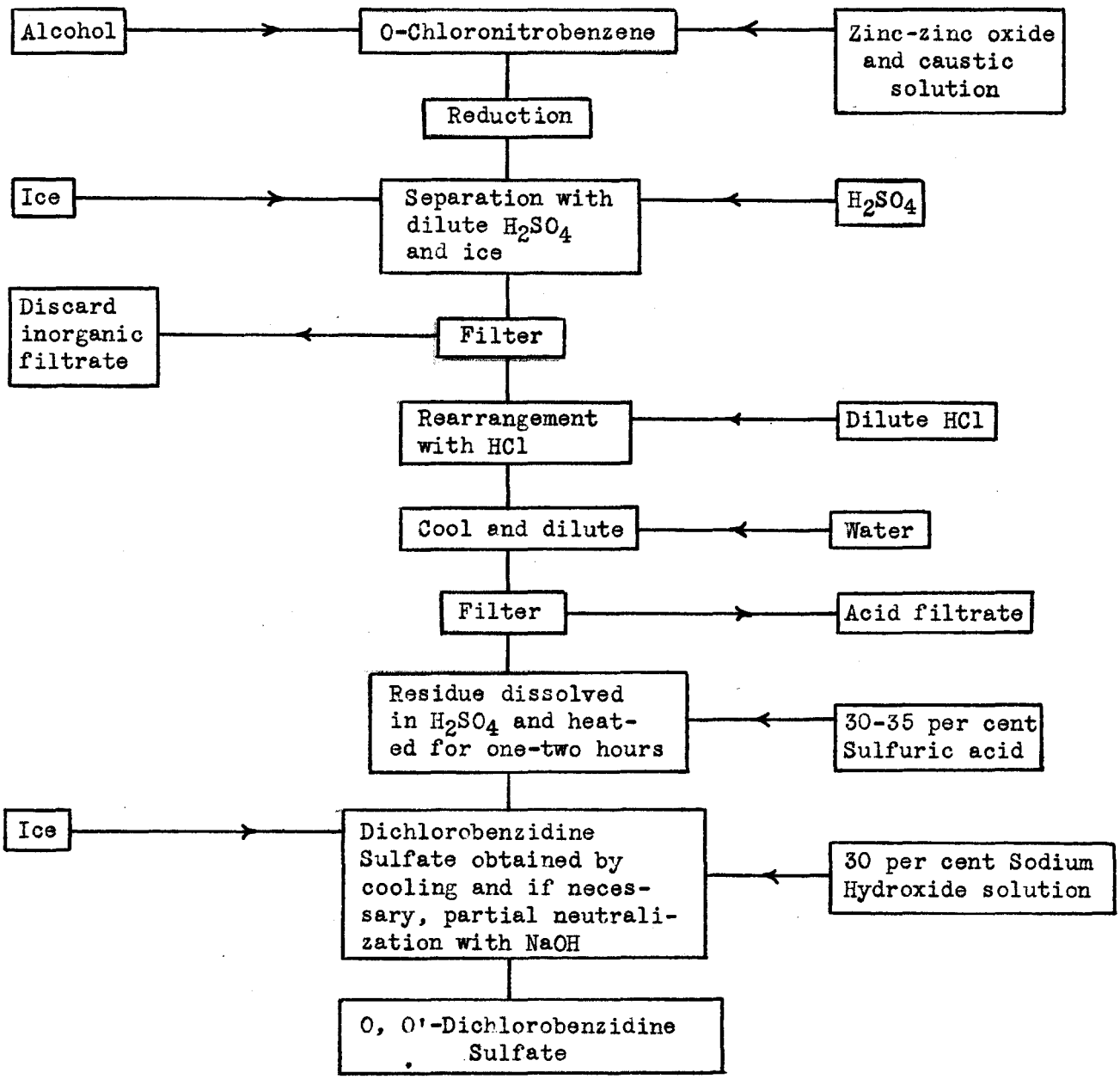
Formation of O, O'-Dichlorobenzidine Sulfate

8. Dissolve the residue in 30-35 per cent sulfuric acid solution, and heat to, or slightly under boiling for one to two hours. The quantity of acid used can be calculated from the solubility curves.

9. Precipitate the o, o'-dichlorobenzidine sulfate by cooling of the solution, and if necessary, also partial neutralization with 30 per cent sodium hydroxide solution.

10. Filter and wash in press with a minimum amount of water to obtain the final product.

Flow Diagram for the Preparation
of O, O'-Dichlorobenzidine Sulfate



COST ESTIMATE OF MATERIALS FOR THE PREPARATION OF O, O'-DICHLOROBENZIDINE SULFATE

A summary of cost data for preparation of a pilot plant batch of o, o'-dichlorobenzidine sulfate is presented below, accompanied by the raw material cost of production per pound of o, o'-dichlorobenzidine sulfate at various yields. Using the amounts of constituent chemicals reported previously, a 100 per cent yield is 9.25 lbs of product.

TABLE XIV
Cost Estimates Per Batch
for the Pilot Plant Production of C, O'-Dichlorobenzidine Sulfate

Constituent	Quantity used per batch lbs	Cost per pound of constituent	Cost per batch
o-Chloronitrobenzene	7.00	0.18	$1.260
Zinc	9.70	0.12	1.165
Zinc oxide	0.88	0.075	0.066
Denatured alcohol	1.06*	0.65*	0.684
Sodium hydroxide	2.65	0.03	0.80
Sulfuric acid	8.43	0.02	0.168
Hydrochloric acid	26.00	0.02	0.520
		Total cost	$3.94

* Reported as gallons

TABLE XV

Variation in Estimated Cost With Yield

Cost per pound of o, o'-dichlorobenzidine sulfate	Yield per cent
$4.26	10
2.13	20
1.42	30
1.07	40
0.85	50
0.71	60
0.61	70
0.53	80
0.48	90
0.43	100

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APPENDIX

TABLE XVI

Data Summary for Laboratory Preparation of O, O'-Dichlorobenzidine

Run No.	$C_6H_4NO_2Cl$ gms	Zn gms	ZnO gms	NaOh gms	H_2O gms	C_2H_5OH (95%) ml	Reduction Time hr
1	79	108	—	10	23	—	$\frac{1}{2}$
2	79	108	—	10	23	—	$2\frac{1}{2}$
3	79	110	—	10	23	200	$2\frac{1}{2}$
4	158	200*	—	160	130	—	9
5	38	60	—	15	35	200	7
6	79	100	—	5	54	64	8
7	79	120	—	18	71	30	7
8	79	100	—	33	66	15	10
9	158	200	—	40	115	120	9
10	79	100	—	80	120	90	3
11	158	240	—	140	205	250	6
12	79	110	—	50	115	55	6
13	79	110	—	65	125	—	$8\frac{1}{2}$
14	158	280	—	55	115	—	9
15	158	100	—	55	75	—	2
16	158	230	—	120	140	150	7
17	158	240	—	100	150	—	8
18	316	510	—	210	360	300	$11\frac{1}{2}$
19	79	140	—	50	120	120	8
20	79	130	—	40	120	70	6
21	79	130	—	40	80	50	8
22	79	150	4	60	130	50	4
23	79	150	4	70	130	50	$6\frac{1}{2}$
24	79	140	4	60	110	50	13
25	79	130	4	50	130	—	12
26	79	135	5	50	220	25	$8\frac{1}{2}$
27	79	130	10	80	180	50	7
28	79	110	10	30	120	50	3

* Reported as gms iron

TABLE XVI
(continued)

Run No.	Extraction Agent ml	Rearranging Acid	Acid Used in Salt Formation	M. P. of final Product °C	Purity of Product Per cent	Yield Per cent
1	—	HCl	—	50	—	—
2	—	HCl	—	50	—	—
3	—	HCl	—	50	—	—
4	—	HCl	—	*	—	—
5	—	HCl	—	*	—	—
6	—	HCl	—	145	—	—
7	—	HCl	—	90	—	—
8	—	HCl	—	*	—	—
9	—	HCl	—	160	—	—
10	—	HCl	—	127	—	—
11	—	HCl	—	140	—	—
12	—	H_2SO_4	—	70	—	—
13	—	HCl	—	*	—	—
14	—	HCl	—	*	—	—
15	—	HCl	—	*!	—	—
16	C_6H_6 100	HCl	—	132	—	—
17	C_6H_6 100	HCl	—	*!	—	—
18	C_6H_6 100	H_2SO_4	—	110	—	—
19	C_2H_5OH 100	H_2SO_4	H_2SO_4	36	—	—
20	C_2H_5OH 100	H_2SO_4	H_2SO_4	40	—	—
21	C_2H_5OH 100	HCl	H_2SO_4	40-50	—	—
22	C_6H_6 200	HCl	H_2SO_4	212	64	39
23	C_6H_6 250	HCl	H_2SO_4	212	95	38
24	—	HCl	H_2SO_4	212	83	31
25	C_6H_6	HCl	H_2SO_4	195	48	13.7
26	C_6H_6	HCl	H_2SO_4	210	83.5	29
27	C_6H_6	HCl	H_2SO_4	212	96.5	33.5
28	C_6H_6	HCl	H_2SO_4	*	—	16.5

! Flask broke during reaction
* Reaction ended in black tarry residue

Note: Since any material that melted under 150°C was not the desired product, no yield or purity was calculated.

TABLE XVII

Summary Data for Pilot Plant
Preparation of O, O'-Dichlorobenzidine

Run No.	Zn gms	ZnO gms	NaOH gms	H_2O gms	C_2H_5OH cc	$C_6H_4NO_2Cl$ gms	HCl lbs
1-P	4400	400	1200	6600	2100	3160	24
2-P	4400	400	1654	4000	2500	3160	36
3-P	4400	400	1200	11,000	2200	3160	27
4-P	4400	400	1200	10,700	2000	3160	25

TABLE XVII (continued)

Run No.	H_2SO_4 lbs	C_6H_6 cc	Reaction Time Hr	M.P. °C	Purity Per cent	Yield Per cent
1-P	—	7000	4.5	125	—	—
2-P	—	—	6	195	56	19.6
3-P	11.5	—	8	200	—	0.5
4-P	8	—	11	210	100	14

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VITA

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